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ANALYSIS OF THE Np(IV) OXALATE SEMI-CONTINUOUS PRECIPITATION PROCESS

INTRODUCTION

The neptunium recovered in 200 Area processing is precipitated as Np(IV) oxalate, then the Np(IV) oxalate is calcined to NpO_2. The NpO_2 is blended with aluminum powder, and the blend fabricated into target elements for reactor irradiation to produce ^{238}Pu. The precipitation step is critical to this processing sequence – the Np(IV) oxalate should filter well, should have a low solubility to minimize losses, recycle, etc., and should calcine to yield a NpO_2 product with an acceptable particle size range and distribution to blend satisfactorily with powdered aluminum.

In a previous letter,[1] a semi-continuous, multistage precipitation flowsheet was recommended for Phase II of the new HB-Line. A multistage precipitation system offers the flexibility needed to control neptunium oxide characteristics through any future variations in neptunium feed streams and/or fuel fabrication conditions

(different fuel loadings, aluminum blending powder uniformity requirements, etc.). Precipitation of Np(IV) oxalate would take place in three stages: a premixer step, to produce nuclei for subsequent crystal growth; a bulk precipitation step, where the nuclei grow essentially to the desired particle size; and a final digestion step to complete the precipitation and reduce loss to the filtrate. Concentrations, flow rates, and residence times in the first two steps must be accurately controlled to give a specified product.

This report contains a detailed analysis of the process variables that led to the development of the proposed flowsheet.[1] This analysis can be utilized for selection of equipment sizes, instrument ranges, and other process requirements. The process equipment, streams, etc., are shown in Figure 1.

SUMMARY

A mathematical model was developed for a three-stage precipitation process for neptunium(IV) oxalate to relate equipment requirements to process variables. Process operating conditions were chosen over reasonable maximum and minimum ranges to define vessel sizes, instrument ranges, and other control ranges. The schematic flow diagram is shown in Figure 1; a set of sample flowsheet values, utilized for design purposes, is given in Table 1.

DISCUSSION

General

The analysis reported here was undertaken to provide a basis for equipment sizes and instrumentation requirements for precipitation equipment for the new H-Area B-Line. Laboratory studies (in progress) will define the actual operating conditions necessary to produce NpO_2 with a given specified particle size range and morphology. This analysis arbitrarily chooses conditions that require maximum equipment sizes and instrumentation ranges, to ensure that any later flowsheet requirements can be met.

The solubility of Np(IV) oxalate is a function of the free oxalate ion in solution, which in turn depends on the ratio $[H_2C_2O_4]/[HNO_3]^2$ in mixed oxalic acid-nitric acid solutions because oxalic acid is a weak acid.[2] The Np(IV) solubility in these mixed solutions is given in Figure 2 as a function of the above ratio, designated R_s. The precipitation is assumed to be made in the oxalate-rich solubility region ($R_s > 0.02$, right side of Figure 2), where the high oxalate, dilute nitric system results in maximum precipitator volume. From the stoichiometry of the

precipitation reaction and from material balance in each of the precipitation steps, a mathematical model of the semi-continuous precipitation process is developed to aid in calculating flow rates and necessary feed concentrations.

Premixer

The premixer handles a fraction of the main neptunium stream and operates in the region of lowest solubility to produce crystal nuclei that subsequently will grow in size in the primary precipitator. Two streams [neptunium(IV) nitrate (Stream 1A), and oxalic acid (Stream 2)] enter the premixer. The premixer is assumed to have a very small residence volume and short residence time and will process no more than ten percent (10%) of the total neptunium stream. The effluent from the premixer (Stream 3) flows into the primary precipitator. From the precipitation reaction

$$Np(NO_3)_4 + 2\ H_2C_2O_4 \rightarrow Np(C_2O_4)_2 + 4\ HNO_3 \tag{1}$$
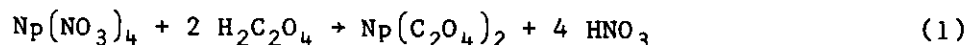
and a material balance for the streams flowing into the premixer, Equation 2 can be derived (see Appendix I for the derivation). This equation gives the relation between solution concentrations and flow rates to establish solubility conditions favorable for the generation of neptunium oxalate crystal nuclei.

$$(R_s)_{PM} \left[\frac{\dot{V}_{1A}[HNO_3]_{1A} + \dot{V}_2[HNO_3]_2 + 4[Np^{+4}]_{1A}\ \dot{V}_{1A}}{\dot{V}_2 + \dot{V}_{1A}} \right]^2$$

$$= \left[\frac{\dot{V}_2\ [H_2C_2O_4]_2 - 2\ \dot{V}_{1A}[Np^{+4}]_{1A}}{\dot{V}_2 + \dot{V}_{1A}} \right] \tag{2}$$

In Equation 2, $\dot{V}$ is the flow rate of a process stream, the bracketed chemical symbols are molar concentrations, and R_s is the parameter $[H_2C_2O_4]/[HNO_3]^2$ which determines the solubility of neptunium. The subscripts (e.g., the subscript "1A" in $\dot{V}_{1A}$) refer to a feed stream from Figure 1.

With all other parameters specified, Equation 2 can be solved for $\dot{V}_2$, the flow rate of the oxalic acid precipitant. Table 2 shows values for $\dot{V}_2$ for $(R_s)_{PM} = 0.08$ (a point of low Np solubility), for cold feed HNO_3 concentrations of 0, 1, and 2M HNO_3 and 0.2 to 1.0M $H_2C_2O_4$, and at a specified neptunium feed

rate ($\dot{V}_{1A}$) of 0.03 L/m. These values are shown graphically
in Figure 3. For normal operation, the oxalic acid precipitant
will be 0.9M with low nitric acid concentration. It was therefore
recommended that the instrumentation measuring range be 0.01-0.3
L/min, (as indicated in Reference 1).

With the selection of a different control point for neptunium
solubility in the premixer, the new value of R_s would result in a
new set of values for Table 2. However, the solubility parameter
values selected, $(R_s)_{PM} = 0.08$, represents an oxalate-rich system
that is regarded as a reasonable estimate of an upper operating limit
for the premixer.

Primary Precipitator

The primary precipitator is a 4-liter vessel, designed to
provide optimum mixing conditions for the semi-continuous precipi-
tation of 900 gram of Np(IV) oxalate. The vessel size was
selected to give a mean residence time (τ) in the range of 3 to 7
min. See Table 4. The precipitator is seeded with Np(IV) oxalate
nuclei from the premixer, and operating conditions are selected in
a region of moderate solubility to promote and control growth on
these nuclei. The effluent from the premixer (Stream 3), the main
feed of neptunium nitrate solution (Stream 1B), and oxalic acid
(Stream 8) flow into the primary precipitator. The primary pre-
cipitator overflows into the secondary precipitator (via Stream 4).

From material balance, Equation 3 is derived (see Appendix II
for the derivation).

$$\left[\frac{\dot{V}_3[H_2C_2O_4]_3 + \dot{V}_8[H_2C_2O_4]_8 - 2\,\dot{V}_{1B}[Np^{+4}]_{1B}}{\dot{V}_3 + \dot{V}_{1B} + \dot{V}_8} \right] = \tag{3}$$

$$(R_s)_{P1}\left[\frac{\dot{V}_{1B}[HNO_3]_{1B} + \dot{V}_8[HNO_3]_8 + \dot{V}_3[HNO_3]_3 + 4[Np^{+4}]_{1B}\,\dot{V}_{1B}}{\dot{V}_3 + \dot{V}_8 + \dot{V}_{1B}} \right]^2$$

As before, each $\dot{V}$ represents a flow rate, the bracketed
formulas are molar concentrations, and R_s is the neptunium solu-
bility parameter $[H_2C_2O_4]/[HNO_3]^2$. The subscripts indicate the
stream numbers from Figure 1.

From Equation 3, $\dot{V}_8$, the oxalic/nitric acid flow rate to the primary precipitator, can be determined for specified values of R_s. Values of $\dot{V}_8$ were calculated with this feed stream containing HNO_3 concentrations of 0 and 0.5M and $H_2C_2O_4$ concentrations of 0.1 to 1M. The results are shown in Table 3 and 4, and Figures 4 and 5. It was therefore recommended that the instrumentation measuring range be 0.05 – 1.0 L/min (indicated in Reference 1). Table 4 shows required $\dot{V}_8$ values for other probable oxalate-rich solubility operating conditions.

Table 4 shows the calculated mean residence times (τ) in the primary precipitator for a range of R_s values from 0.1 to 2.0 and the influence of oxalic and nitric acid concentrations upon flow rates into the primary precipitator. These results are shown graphically in Figures 6 and 7.

The mean residence time required in the primary precipitator is determined by selecting the appropriate oxalic/nitric acid feed composition, i.e. flow rate. The time-dependent values for $[HNO_3]_{P1}$ and $[H_2C_2O_4]_{P1}$ were calculated from the following equations, derived in Appendix II.

$$[HNO_3]_{P1} = [HNO_3]_{P1}^o \exp -\left(\frac{\dot{V}_4 t}{V_{P1}}\right)$$

$$+ \left[\frac{\dot{V}_{1B}[HNO_3]_{1B} + \dot{V}_8[HNO_3]_8 + \dot{V}_3[HNO_3]_3 + 4\,\dot{V}_{1B}[Np^{+4}]_{1B}}{\dot{V}_4}\right]* \quad (4)$$

$$\cdot \left[1 - \exp -\left(\frac{\dot{V}_4 t}{V_{P1}}\right)\right]$$

where, in addition to symbols previously described, V_{P1} is the residence volume of the primary precipitator, and $[HNO_3]_{P1}^o$ and $[H_2C_2O_4]_{P1}^o$ are the initial nitric and oxalic acid concentrations in the primary precipitator, respectively.

Similarly, the oxalic acid concentrations is given by

$$[H_2C_2O_4] = [H_2C_2O_4]_{P1}^o \exp -\left(\frac{\dot{V}_4 t}{V_{P1}}\right) +$$

$$\left[\frac{\dot{V}_3[H_2C_2O_4]_3 + \dot{V}_8[H_2C_2O_4]_8 - 2\,\dot{V}_{1B}[Np^{+4}]_{1B}}{\dot{V}_4}\right] *$$ (5)

$$\left[1 - \exp -\left(\frac{\dot{V}_4 t}{V_{P1}}\right)\right]$$

where $\dot{V}_4 = \dot{V}_{1B} + \dot{V}_3 + \dot{V}_8$

The steady-state values for nitric and oxalic acid can be obtained from these equations by allowing the time (t) to be very large so that the exp $(-\dot{V}_4 t/V_{P1}) = 0$. The approach to steady-state for $(R_s)_{P1} = 1.0$, $[H_2C_2O_4]_{P1} = 0M$, $[HNO_3]_{P1} = 0.74$ $\dot{V}_4 = 1.27$ L/m is shown in Figure 8.

Crystal nucleation and growth rates are strong functions of the degree of supersaturation. The primary precipitator is designed to operate with an appreciable degree of supersaturation, defined as the instantaneous percentage of neptunium(IV) in solution above the equilibrium solubility.[3,4,5] The degree of supersaturation can be calculated by Equation 6 as found in Reference 5.

$$S_s^o = \frac{[Np^{+4}]_{P1}^{IMC} - [Np^{+4}]_{P1}^{EQ.}}{[Np^{+4}]_{P1}^{EQ}} (100)$$ (6)

The results of this calculation are shown in Figure 9, and were obtained by combining Equation 6 with Equation 36 in Appendix II. Figure 9 shows that within seconds, an appreciable degree of supersaturation is obtained providing a good driving force for crystal nucleation and growth.

Secondary Precipitator

In the secondary precipitator, cold feeds are added to reach the minimum solubility conditions for Np(IV) oxalate so that losses to the filtrate will be low. The flow rates of these feeds are not critical when the system is operated in the semicontinuous mode, since only the solubility adjustment is performed. However, the flow rate ranges specified in Reference 1 were set to allow operation of the secondary precipitator in the batch mode. In the semi-continuous mode, the adjustment streams may be added simultaneously with the overflow from the primary precipitator, or to the entire

batch at the end of the normal precipitation run. The final solution concentrations are shown on the flowsheet material balance (Table 1). The equations used to calculate the required volume of the solubility adjustment feed solution, are derived in Appendix III. Concentrations for the solubility adjustment solutions must be carefully selected depending upon whether the precipitation is in the oxalate rich or lean solubility region.

REFERENCES

1. J. D. Livingston, "Recommended Flowsheet For New HB-Line Neptunium Precipitation Facilities," DPST-80-664, November 1980.

2. J. A. Porter, "Precipitation of Neptunium Oxalate and Calcination to Neptunium Oxide," DP-591, July 1961.

3. A. D. Randolph and M. A. Larson, "Theory of Particulate Processes," Academic Press, p. 84, 1971.

4. A. D. Randolph, "How to Approach Problems of Crystallization," Chem. Engr., May 4, 1970.

5. J. W. Mullin, "Crystallization," Butterworth & Co., p. 28 1961.

TABLE 1

Representative Flowshseet, Steady-State Values

Stream	$[HNO_3]$, M	$[H_2C_2O_4]$, M	$[Np^{+4}]$, M	$[Np(C_2O_4)_2]$, M	$[C_6H_8O_6]$, M	Flow Rate $(\dot{V})$, L/min
1A	2	0	0.21	0	0.042	0.03
1B	2	0	0.21	0	0.042	0.3
2	0	0.9	0	0	0	0.03
3	1.52	0.19	2.95×10^{-5}	0.113	0.02	0.06
4	0.74	0.55	1.22×10^{-4}	0.055	0.011	1.27
6	3.05	0.45	2.53×10^{-5}	0.043	0.009	Vacuum trans.
7	14.0	0	0	0	0	1.0*
8	0	0.9	0	0	0	0.91
10	1.0	0.05	0	0	0	10.0**

* To be added at 1 L/min for 17 min after P1 is emptied into P2

** Total volume added (liters)

NOTES:

Total volumetric throughput/batch = 97.2 liters

Cycle time/batch = 60 minutes = t_c

Basis for flowsheet = 1000 gr Np^{237}

TABLE 2

Oxalic Acid Feed Flowrate to Premixer for Various Oxalic Acid and Nitric Acid Concentrations

$(R_s)_{PM} = 0.08$

$[H]_2 = 0M$		$[H]_2 = 1.0M$		$[H]_2 = 2.0M$	
$[B]_2$, (M)	$\dot{V}_2$, (L/m)	$[B]_2$, (M)	$\dot{V}_2$, (L/m)	$[B]_2$, (M)	$\dot{V}_2$, (L/m)
0.2	0.098	0.2	0.232	0.2	52.338
0.3	0.070	0.3	0.129	0.3	9.793
0.4	0.055	0.4	0.091	0.4	0.429
0.6	0.040	0.6	0.057	0.6	0.122
0.8	0.031	0.8	0.042	0.8	0.072
0.9	0.029	1.0	0.034	1.0	0.051
1.0	0.026				

where: $[HNO_3] \equiv [H]$

$[H_2C_2O_4] \equiv [B]$

TABLE 3

Oxalic Acid Feed Flow Rate to Primary Precipitator for Various
Oxalic and Nitric Acid Concentrations

$(R_s)_{P1} = 1.0$

$[H]_8$ = OM		$[H]_8$ = 0.5M	
$[B]_8$, (M)	$\dot{V}_8$, (L/m)	$[B]_8$, (M)	$\dot{V}_8$, (L/m)
0.1	3.47	0.1	∞
0.2	2.273	0.2	∞
0.3	1.778	0.3	∞
0.4	1.494	0.4	∞
0.6	1.168	0.6	3.241
0.8	0.979	0.8	2.185
0.9	0.91	0.9	1.894
1.0	0.853	1.0	1.678

TABLE 4

Influence of Solubility Parameter on Oxalic Acid Feed Flow Rate and
Mean Residence Time for the Primary Precipitator

R_s^{SREC}	$[B]_8$ (M)	$[H]_8$ (M)	$\dot{V}_3$ (L/m)	$\dot{V}_8$ (L/m)	$[H]_4$ (M)	$[B]_4$ (M)	R_s^{CALC}	$\dot{V}_4$ (L/m)	τ (min)
0.1	0.9	0	0.062	0.282	1.47	0.22	0.1	0.644	6.2
0.2	0.9	0	0.062	0.392	1.26	0.32	0.2	0.754	5.3
0.4	0.9	0	0.062	0.560	1.03	0.42	0.4	0.922	4.3
0.6	0.9	0	0.062	0.694	0.897	0.480	0.6	1.171	3.4
0.8	0.9	0	0.062	0.809	0.81	0.52	0.8	1.171	3.4
1.0	0.9	0	0.062	0.911	0.744	0.55	1.0	1.273	3.1
1.5	0.9	0	0.062	1.13	0.64	0.61	1.5	1.492	2.7
2.0	0.9	0	0.062	1.32	0.57	0.64	2.0	1.678	2.4
0.1	0.9	0.5	0.062	0.326	1.62	0.26	0.1	0.688	5.8
0.2	0.9	0.5	0.062	0.498	1.39	0.39	0.2	0.860	4.7
0.4	0.9	0.5	0.062	0.820	1.15	0.53	0.4	1.182	3.4
0.8	0.9	0.5	0.062	1.503	0.91	0.67	0.8	1.865	2.1
1.0	0.9	0.5	0.062	1.895	0.84	0.71	1.0	2.257	1.8
1.5	0.9	0.5	0.062	3.145	0.72	0.78	1.5	3.507	1.1
2.0	0.9	0.5	0.062	5.108	0.64	0.82	2.0	5.470	0.73
0.1	0.6	0	0.062	0.390	1.26	0.16	0.1	0.752	5.3
0.2	0.6	0	0.062	0.527	1.07	0.23	0.2	0.889	4.5
0.4	0.6	0	0.062	0.736	0.86	0.29	0.4	1.098	3.6
0.8	0.6	0	0.062	1.043	0.67	0.36	0.8	1.405	2.8
1.0	0.6	0	0.062	1.168	0.62	0.38	1.0	1.53	2.6
1.5	0.6	0	0.062	1.438	0.53	0.41	1.5	1.8	2.2
2.0	0.6	0	0.062	1.666	0.47	0.44	2.0	2.028	1.9

TABLE 4 (continued)

R_s^{SREC}	$[B]_8,$ (M)	$[H]_8,$ (M)	$\dot{V}_3,$ (L/m)	$\dot{V}_8,$ (L/m)	$[H]_4,$ (M)	$[B]_4,$ (M)	R_s^{CALC}	$\dot{V}_4,$ (L/m)	τ (min)
0.1	0.6	0.5	0.062	0.471	1.418	0.20	0.1	0.833	4.8
0.2	0.6	0.5	0.062	0.718	1.208	0.292	0.2	1.08	3.7
0.4	0.6	0.5	0.062	1.213	0.986	0.389	0.4	1.575	2.54
0.8	0.6	0.5	0.062	2.423	0.775	0.480	0.8	2.785	1.44
1.0	0.6	0.5	0.062	3.242	0.712	0.507	1.0	3.604	1.11
1.5	0.6	0.5	0.062	6.773	0.607	0.553	1.5	7.135	0.56
2.0	0.6	0.5	0.062	18.897	0.539	0.582	2.0	19.259	0.20

DESCRIPTION OF ABBREVIATIONS IN FIGURE 1

Item	Description
PM	Premixer
P1	Primary Precipitator
P2	Secondary Precipitator
1A	Actinide Feed Stream to Premixer
1B	Actinide Feed Stream to Primary Precipitator
1C	Actinide Feed Stream to Secondary Precipitator
2	Oxalic/Nitric Acid Feed to Premixer (Cold Feed #1))
3	Discharge from Premixer to Primary Precipitator
4	Discharge Overflow from Primary to Secondary Precipitator
5	Decant Stream of Primary to Secondary Precipitator
6	Transfer from Secondary Precipitator to Filter Station
7	Oxalic/Nitric Acid Feed to Secondary Precipitator (Cold Feed #2)
8	Oxalic/Nitric Acid Feed to Primary Precipitator (Cold Feed #2)
9	Filtrate Discharge to Catch Tank
10A	Wash Solution to Secondary Precipitator
10B	Wash Solution to Filter Station
11	Flush Solution to Premixer

PRECIPITATION PROCESS FLOW DIAGRAM
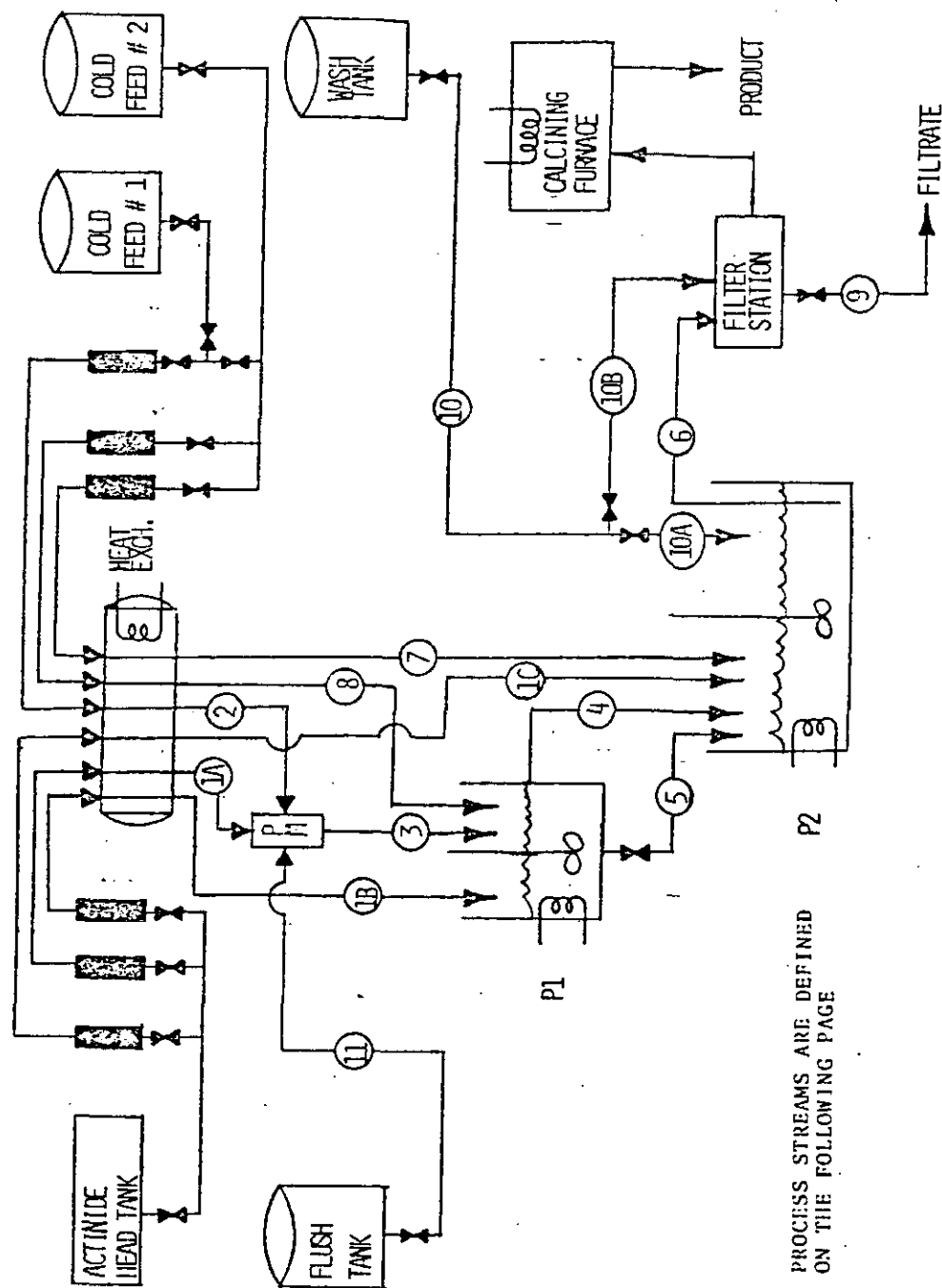
PROCESS STREAMS ARE DEFINED
ON THE FOLLOWING PAGE

FIGURE 3

SOLUBILITY OF $N_P(IV)$ OXALATE

S, (MGR, N_P^{+4}/LITER)

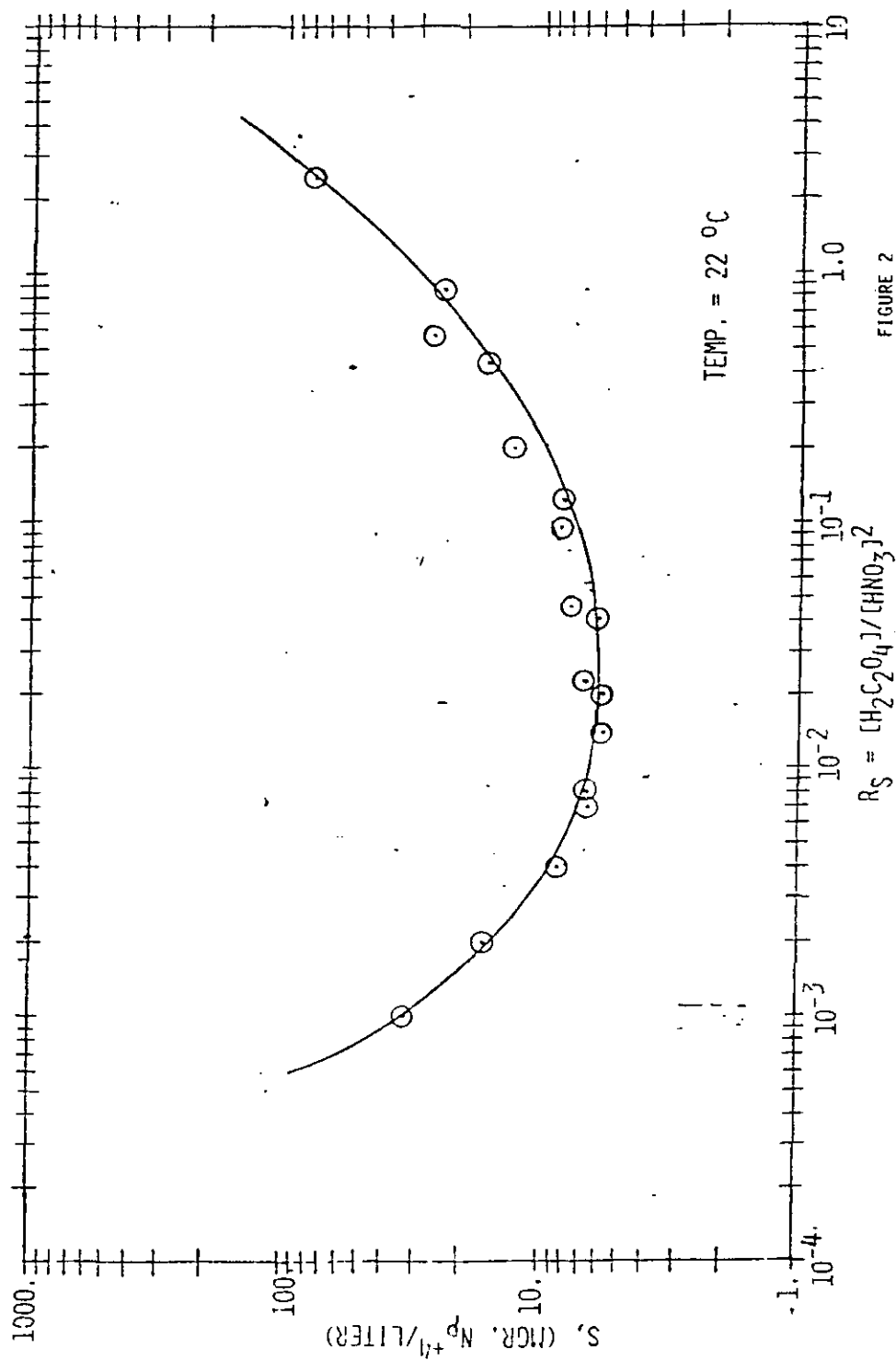$R_S = [H_2C_2O_4]/[HNO_3]^2$

TEMP. = 22 °C

FIGURE 2

FIGURE 3

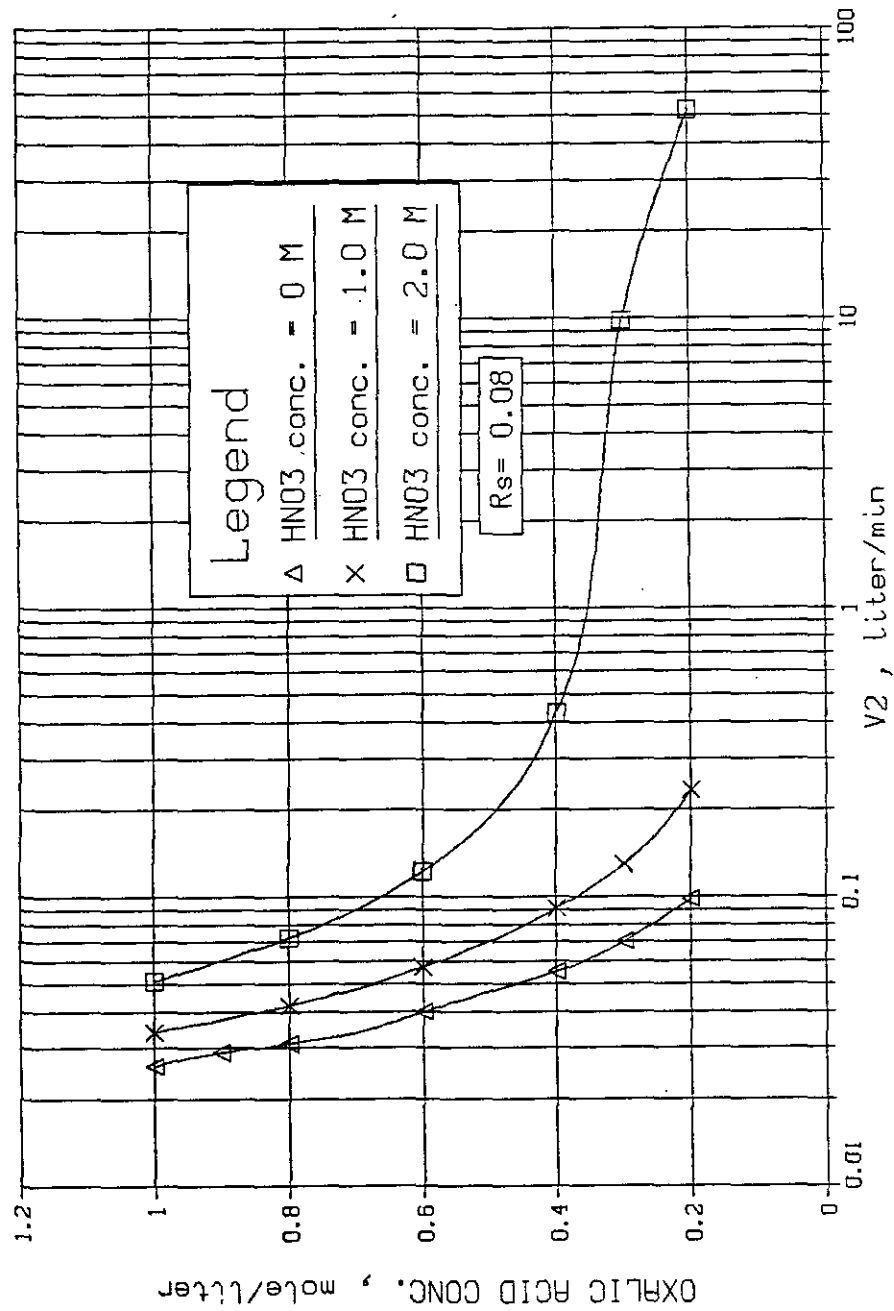OXALIC ACID FEED TO PREMIXER
FLOW RATE VERSUS CONCENTRATION

FIGURE 4

OXALIC ACID FEED TO PRIMARY PRECIPITATOR
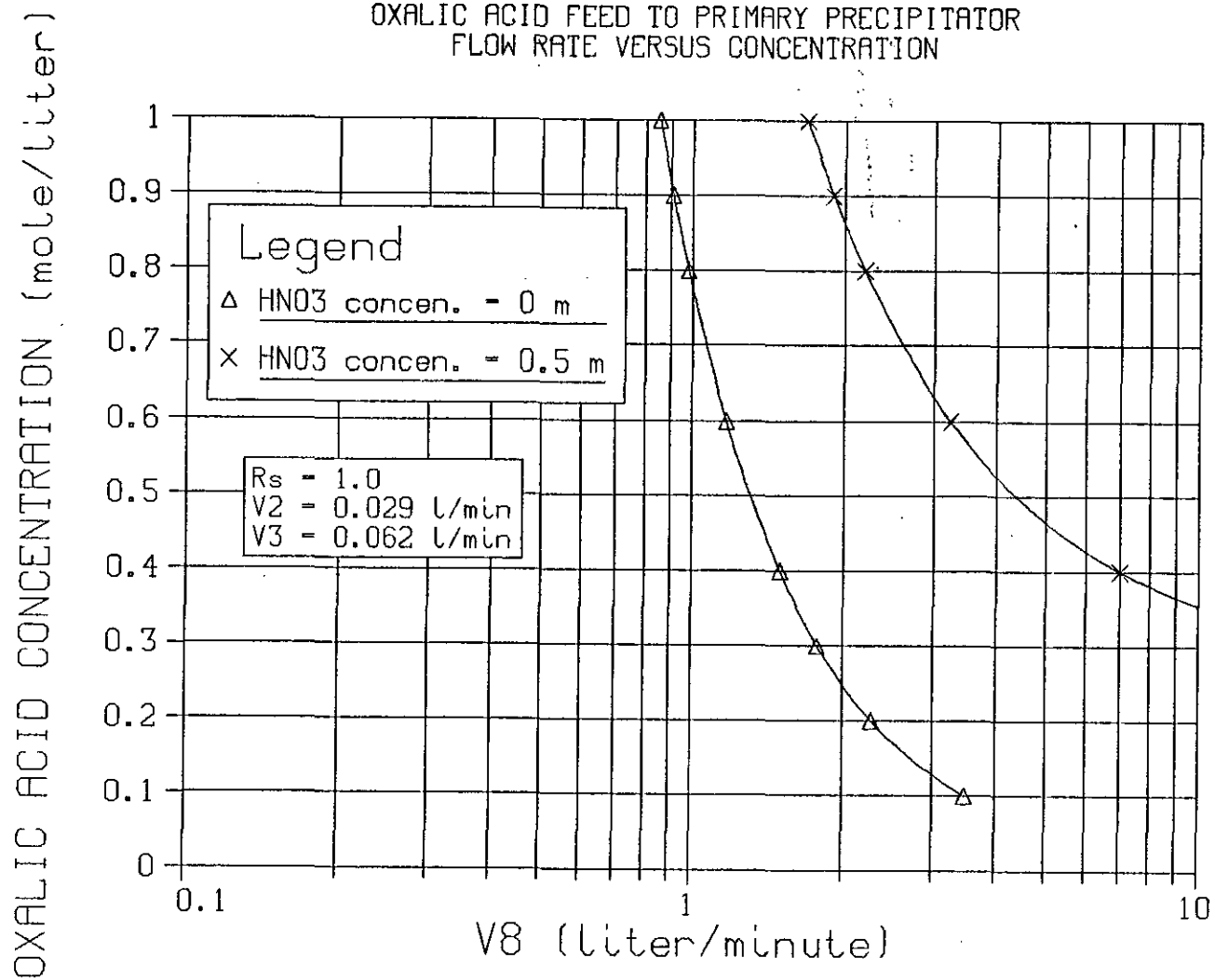FLOW RATE VERSUS CONCENTRATION

FIGURE 5
SOLUBILITY PARAMETER VERSUS
OXALIC ACID FEED FLOW RATE
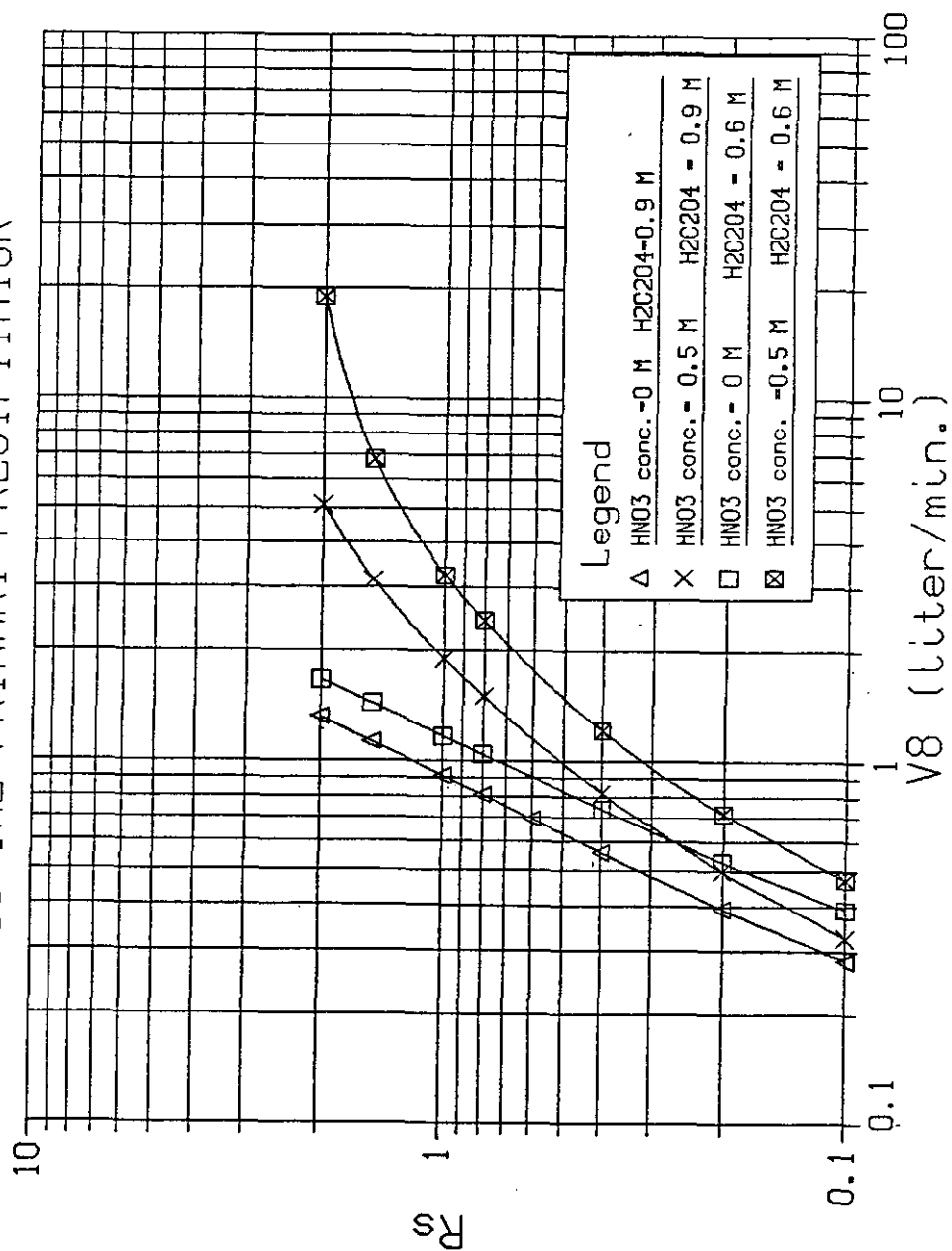TO THE PRIMARY PRECIPITATOR

Legend
△ HNO3 conc.-0 M H2C2O4-0.9 M
× HNO3 conc. - 0.5 M H2C2O4 - 0.9 M
□ HNO3 conc.- 0 M H2C2O4 - 0.6 M
⊠ HNO3 conc. -0.5 M H2C2O4 - 0.6 M

FIGURE 6

PRIMARY PRECIPITATOR: DISCHARGE FLOW RATE AND
RESIDENCE TIME VERSUS SOLUBILITY PARAMETER

COLD FEED COMPOSITION
TO PRIMARY PRECIPITATOR

$\diamondsuit$ $[HNO_3]_8 = 0$ $\underline{M}$, $[H_2C_2O_4]_8 = 0.9$ $\underline{M}$

$\odot$ $[HNO_3]_8 = 0.5$ $\underline{M}$, $[H_2C_2O_4]_8 = 0.9$ $\underline{M}$

$R_S = [H_2C_2O_4]/[HNO_3]^2$

τ (min.)

$\dot{V}_4$ (LITER/MIN)
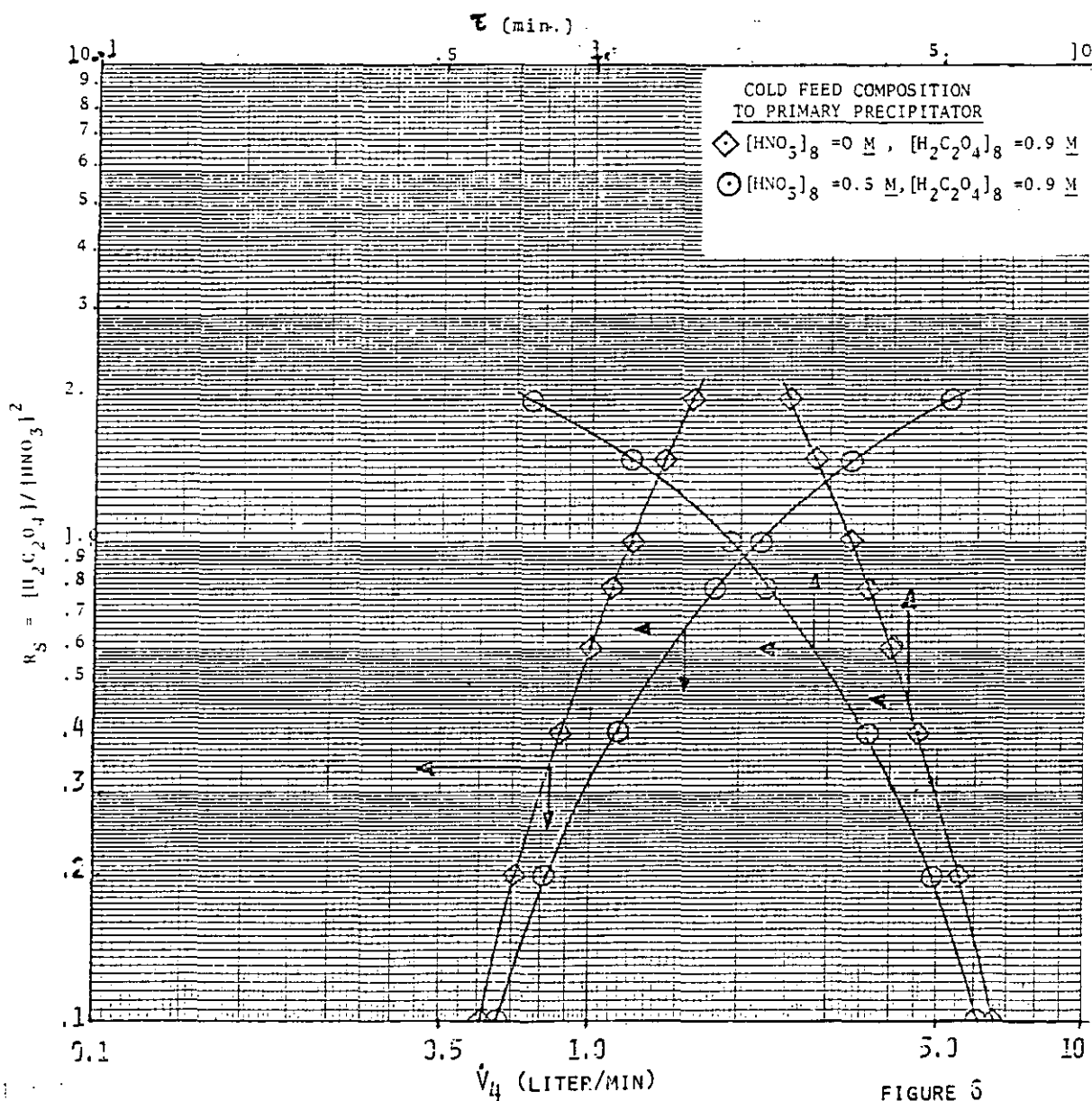
FIGURE 6

FIGURE 7

PRIMARY PRECIPITATOR: DISCHARGE FLOW RATE AND RESIDENCE TIME VERSUS SOLUBILITY PARAMETER

τ (min.)

COLD FEED COMPOSITION
TO PRIMARY PRECIPITATOR

$\triangle$ $[HNO_3]_8 = 0$ $\underline{M}$, $[H_2C_2O_4]_8 = 0.6$ $\underline{M}$

⬡ $[HNO_3]_8 = 0.5$ $\underline{M}$, $[H_2C_2O_4]_8 = 0.6$ $\underline{M}$

$R_S = [HNO_3]/[H_2C_2O_4]^2$
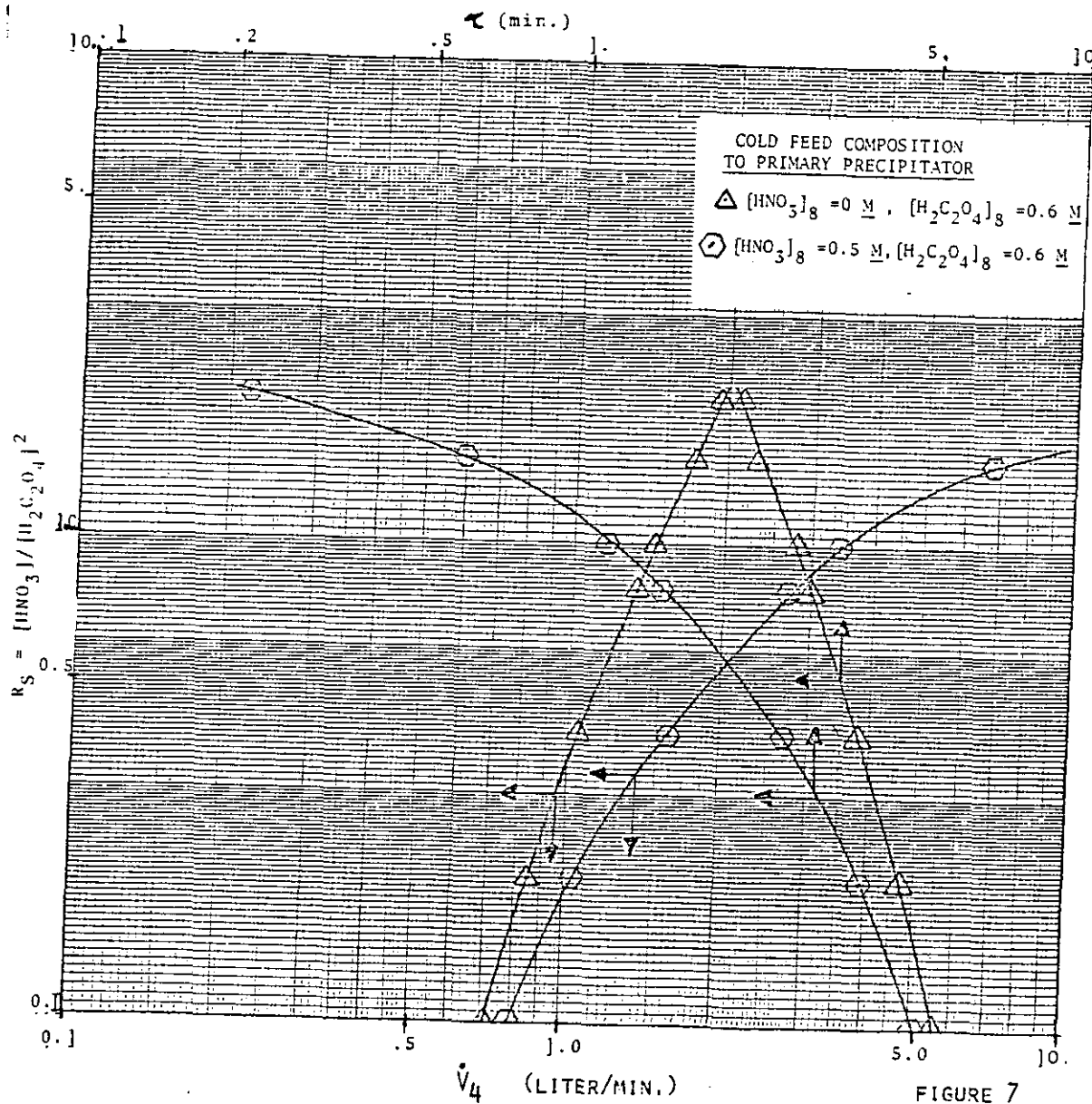
$\dot{V}_4$ (LITER/MIN.)

FIGURE 7

FIGURE 8

PERCENT STEADY-STATE IN PRIMARY PRECIPITATOR VERSUS TIME
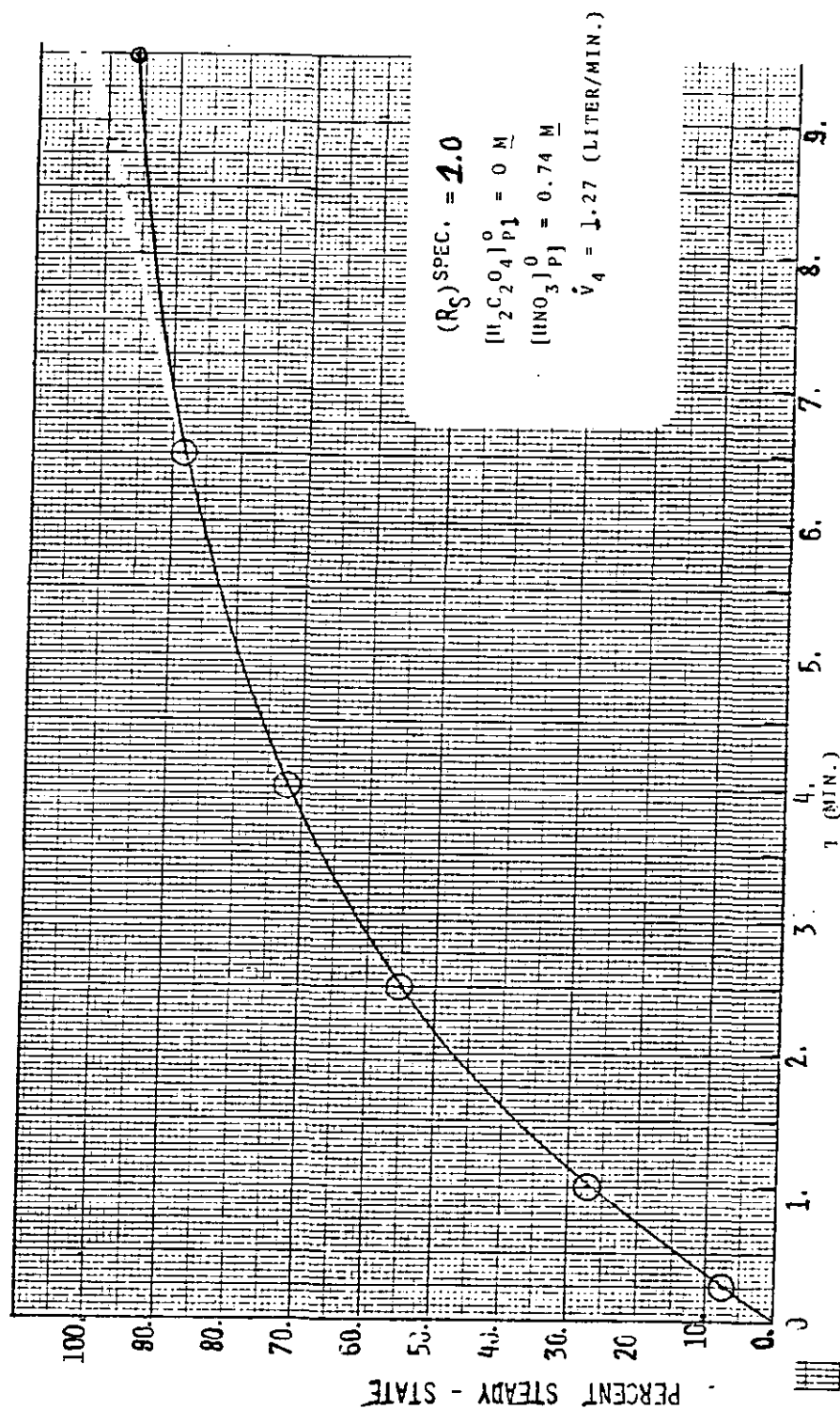
FIGURE 8

FIGURE 9

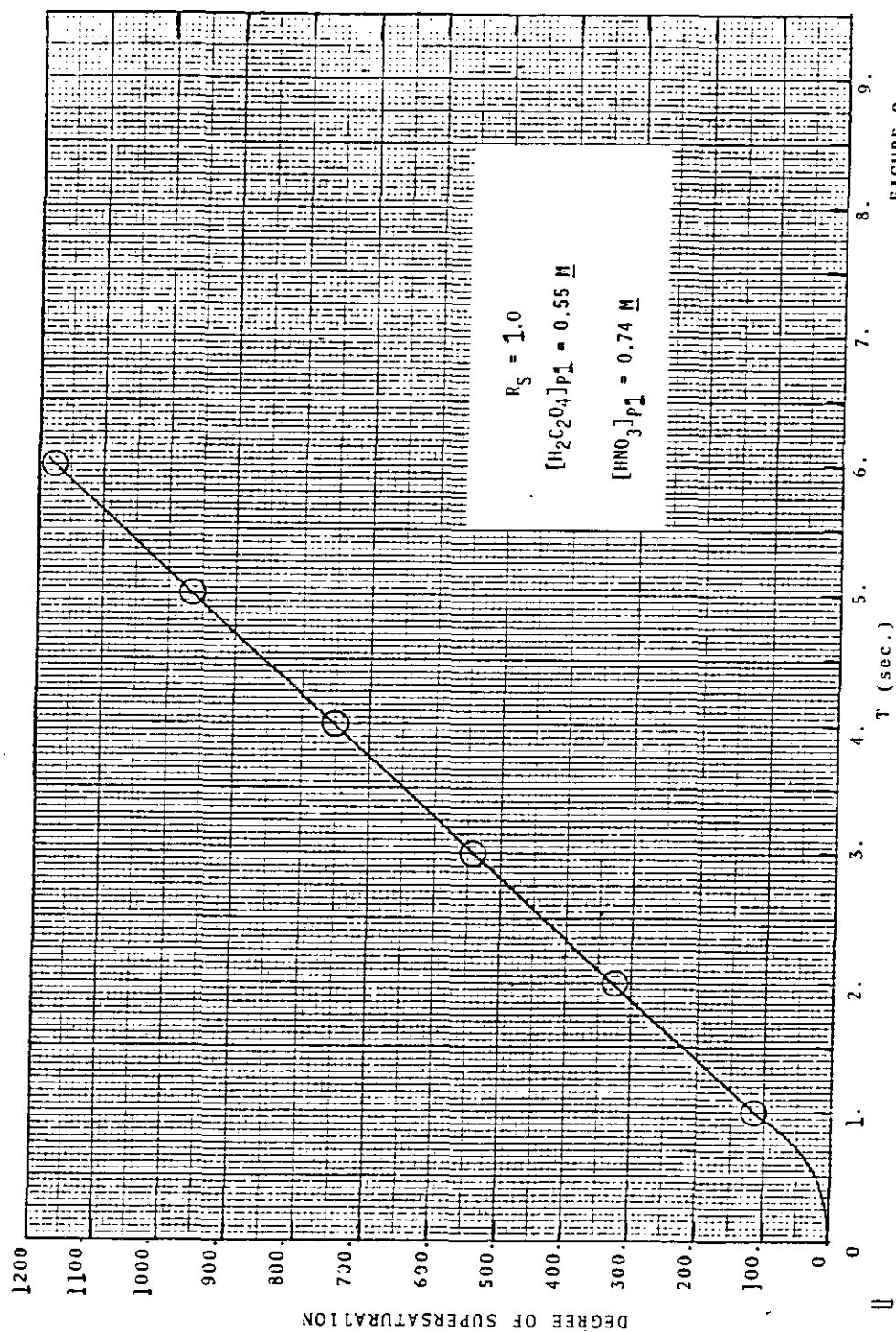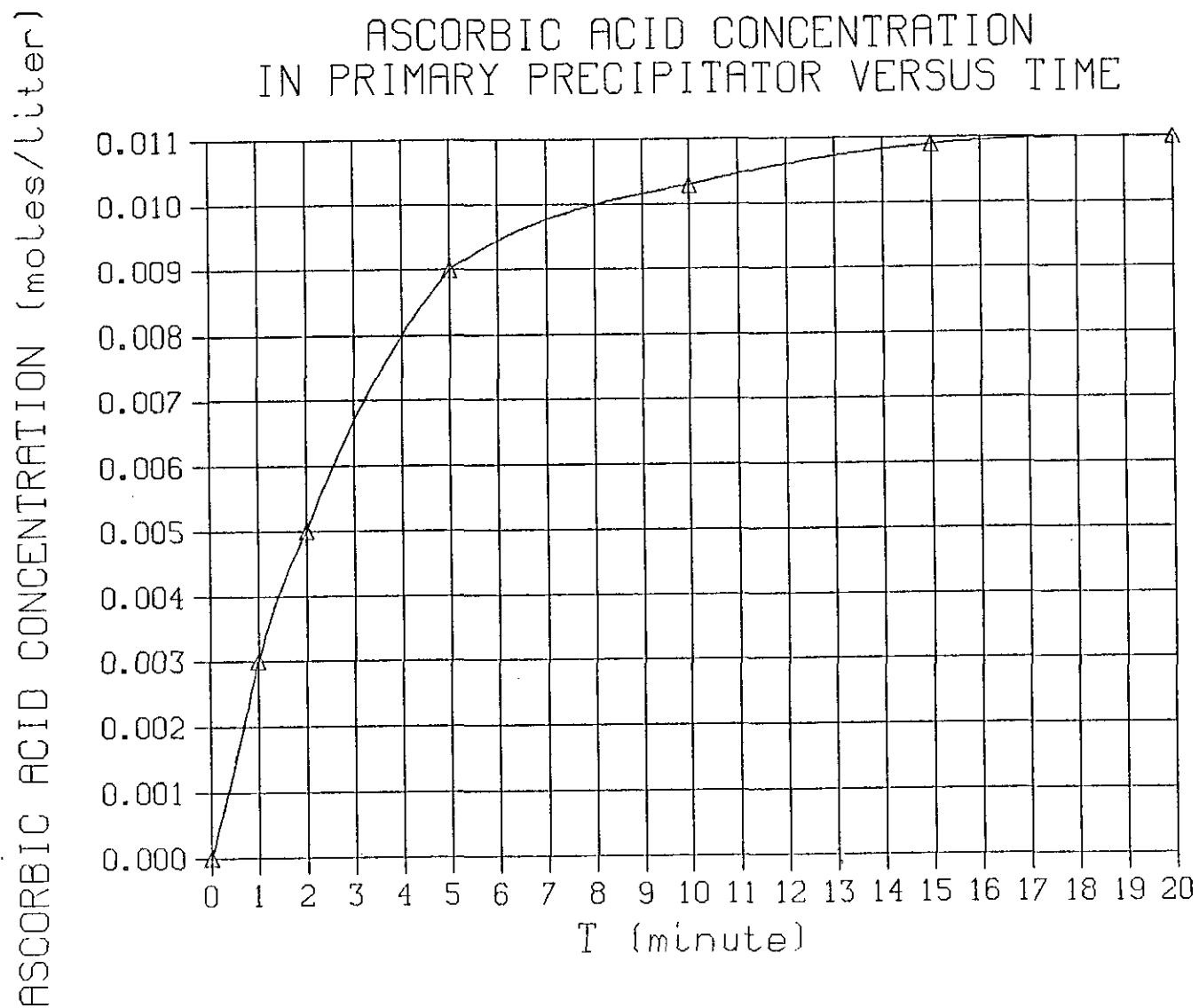## DEGREE OF SUPERSATURATION IN PRIMARY PRECIPITATOR VERSUS TIME

$R_S = 1.0$

$[H_2C_2O_4]_{P1} = 0.55$ $\underline{M}$

$[HNO_3]_{P1} = 0.74$ $\underline{M}$

FIGURE 9

FIGURE 10

ASCORBIC ACID CONCENTRATION
IN PRIMARY PRECIPITATOR VERSUS TIME

APPENDIX I

Material Balance For $[HNO_3]$ In The Premixer

let $[H] \equiv [HNO_3]$

1) $\quad (\dot{M}_H)_i - (\dot{M}_H)_o + (\dot{M}_H)_{gen} = \dfrac{d(M_H)_{PM}}{dt}$

Assuming no (minimal) accumulation:

2) $\quad (\dot{M}_H)_i - (\dot{M}_H)_o + (\dot{M}_H)_{gen} = 0$

Converting the process stream molar flow rates into parameters associated with the premixer

3) $\quad [H]_{1A}\,\dot{V}_{1A} + [H]_2\,\dot{V}_2 - [H]_3\dot{V}_3 + 4.\;[N_p^{+4}]_{1A}\,\dot{V}_{1A} = 0$

4) $\quad [H]_{PM} = [H]_3 = \dfrac{\dot{V}_{1A}[H]_{1A} + \dot{V}_2[H]_2 + 4.\;[N_p^{+4}]_{1A}\,\dot{V}_{1A}}{\dot{V}_2 + \dot{V}_{1A}}$

The above equation results if the premixer is assumed to operate at an ideally instantaneous mixed condition.

Material Balance For $[H_2C_2O_4]$ In The Premixer

let $[B] = [H_2C_2O_4]$

5) $\quad (\dot{M}_B)_i - (\dot{M}_B)_o - (\dot{M}_B)_{RXN} = \dfrac{d(M_B)_{PM}}{dt}$

Assume no accumulation in premixer

6) $\quad \dot{V}_{1A}[B]_{1A} + \dot{V}_2[B]_2 - \dot{V}_3[B]_3 - 2\,\dot{V}_{1A}[N_p^{+4}]_{1A} = 0$

Assuming $[B]_{1A} = 0$

and that the premixer operates at ideally mixed conditions

7) $\quad [B]_{PM} = [B]_3 = \dfrac{\dot{V}_2[B]_2 - 2\,\dot{V}_{1A}[N_p^{+4}]_{1A}}{\dot{V}_2 + \dot{V}_{1A}}$

The solubility of neptunium(IV) in nitric and oxalic acid solutions is expressed in terms of the solubility parameter, $R_s = [H_2C_2O_4]/[HNO_3]^2$, which is temperature dependent.

Rearranging the solubility parameter:

8) $[H_2C_2O_4] = R_s [HNO_3]^2$

Relating equations 4, 7, and 8 we find:

9) $$\left(R_s\right)_{PM} \left[\frac{\dot{V}_{1A}[H]_{1A} + \dot{V}_2 [H]_2 + 4[N_p^{+4}]_{1A} \dot{V}_{1A}}{\dot{V}_2 + \dot{V}_{1A}}\right]^2 =$$

$$\frac{\dot{V}_2[B]_2 - 2 \dot{V}_{1A}[N_p^{+4}]_{1A}}{\dot{V}_2 + \dot{V}_{1A}}$$

The above equation is used to solve for $\dot{V}_2$ when all other parameters are known or specified.

Material Balance for $[HNO_3]$ In P1

let $[H] = [HNO_3]$

1) $(\dot{M}_H)_i - (\dot{M}_H)_o + (\dot{M}_H)_{gen} = \dfrac{d(M_H)_{P1}}{dt}$

Relating process stream molar flow rates to process parameters:

2) $\dot{V}_{1B}[H]_{1B} + \dot{V}_3[H]_3 + \dot{V}_8[H] - \dot{V}_4[H]_{P1} + 4\,\dot{V}_{1B}[N_p^{+4}]_{1B} = \dfrac{d\left(V_{P1}\,[H]_{P1}\right)}{dt}$

assuming: $[H]_4 = [H]_{P1}$

$V_{P1} = constant$

3) $\dot{V}_{1B}[H]_{1B} + \dot{V}_3[H]_3 + \dot{V}_8\,[H]_8 - \dot{V}_4[H]_{P1} + 4\,\dot{V}_{1B}[N_p^{+4}]_{1B} = V_{P1}\,\dfrac{d[H]_{P1}}{dt}$

Rearranging

4) $\dfrac{d[H]_{P1}}{dt} + \dfrac{\dot{V}_4[H]_{P1}}{V_{P1}} = \dfrac{\dot{V}_{1B}\,[H]_{1B} + \dot{V}_8\,[H]_8 + \dot{V}_3\,[H]_3 + 4\,\dot{V}_{1B}[N_p^{+4}]_{1B}}{V_{P1}}$

The equation given above is a first order linear nonhomogeneous differential equation.

At this point it is convenient to make substitutions to integrate the equation.

5) let $W_1 = \dot{V}_4/V_{P1} = constant$

6) let $W_2 = \dfrac{\dot{V}_{1B}\,[H]_{1B} + \dot{V}_8\,[H]_8 + \dot{V}_3\,[H]_3 + 4\,\dot{V}_{1B}\,[N_p^{+4}]_{1B}}{V_{P1}}$

$$W_2 = \text{constant}$$

7) $\chi = [H]_{P1} = f(t)$

therefore

8) $\dfrac{d\chi}{dt} + W_1\chi = W_2$

Use an integrating factor to solve equation (8).

let $\phi \equiv$ integrating factor

9) $\phi \dfrac{d\chi}{dt} + \phi W_1 \chi = \phi W_2$

10)   if $\phi W_1 = d\phi/dt$

then

11) $\phi \dfrac{d\chi}{dt} + \dfrac{\chi d\phi}{dt} = \phi W_2$

Equation (11) is useful since it reduces to the following form

12) $\phi \dfrac{d\chi}{dt} + \chi d\phi/dt = d(\chi\phi)/dt = W_2\phi$

From Equation (10) the integrating factor can be defined

13) $d\phi/dt = \phi W_1$

14) $\dfrac{d\phi}{\phi} = W_1 dt$

integrating we find

15) $\displaystyle\int \dfrac{d\phi}{\phi} = \int W_1 dt = W_1 \int dt$

16) $\ln \phi = W_1 t$

17) $\phi = \exp(W_1 t)$; integ. const. not necessary since it would be factored out in Equation 9.

Equating (17) and (9)

18) $\frac{d\chi}{dt} \exp(W_1 t) + W_1 \chi \exp(W_1 t) = W_2 \exp(W_1 t)$

Recognizing that Equation (18) is of the form

19) $\frac{d\chi}{dt} \exp(W_1 t) + \chi \frac{d[\exp(W_1 t)]}{dt} = W_2 \exp(W_1 t)$

Equation (19) reduces to the form:

20) $\frac{d[\chi \exp(W_1 t)]}{dt} = W_2 \exp(W_1 t)$

21) $d[\chi \exp(W_1 t)] = W_2 \exp(W_1 t)\, dt$

22) $\int d[(\chi \exp(W_1 t)] = \int W_2 \exp(W_1 t)\, dt$

23) $\chi \exp(W_1 t) = \frac{W_2}{W_1} \exp(W_1 t) + \kappa_1$

where: $\kappa_1 \equiv$ constant of integration

From the initial conditions

24) $\chi = \chi_o = [H]_{P1}^o$ @ $t = 0$

25) $\chi_o = \frac{W_2}{W_1} \exp(W_1(o)) + \kappa_1$

26) $\kappa_1 = \chi_o - W_2/W_1$

27) $\chi \exp(W_1 t) = \dfrac{W_2}{W_1} \exp(W_1 t) + (\chi_o - W_2/W_1)$

28) $\chi = W_2/W_1 + \chi_o \exp(-W_1 t) - \dfrac{W_2}{W_1} \exp(-W_1 t)$

29) $\chi = \chi_o \exp(-W_1 t) + \dfrac{W_2}{W_1}\left(1 - \exp(-W_1 t)\right)$

Resubstituting original parameters

30) $[H]_{P1} = [H]_{P1}^o \exp -\left(\dfrac{\dot{V}_4 t}{V_{P1}}\right) + \left[\dfrac{\dot{V}_{1B}[H]_{1B} + \dot{V}_8[H]_8 + \dot{V}_3[H]_3 + 4\,\dot{V}_{1B}[N_p^{+4}]}{\dot{V}_4}\right] *$

$\left[1-\exp\ -\left(\dfrac{\dot{V}_4 t}{V_{P1}}\right)\right]$

Equation (30) now expressed $[H]_{P1}$ as a function of time.

Material Balance for $[H_2C_2O_4]$ in P1

Let $[B]_{P1} \equiv [H_2C_2O_4]_{P1}$, (M)

31) $(\dot{M}_B)_i - (\dot{M}_B)_o - (\dot{M}_B)_{RXn} = \dfrac{d(M_B)_{P1}}{dt}$

32) $\dot{V}_{1B}[B]_{1B} + \dot{V}_8[B]_8 + \dot{V}_3[B]_3 - \dot{V}_4[B]_4 - 2\,\dot{V}_{1B}[N_p]_{1B} = \dfrac{d\left(V_{P1}[B]_{P1}\right)}{dt}$

Assume $[B]_{1B} = 0$, $[B]_4 = [B]_{P1}$, $V_{P1} = $ constant

Performing similar mathematical manipulation for Equation (32) as for Equation (2), the following equation results:

APPENDIX III

Material Balance for [HNO_3] in P2

Let $H \equiv HNO_3$

1) $$[H]_{P2} = \frac{V_7[H]_7 + [H]_4\, V_4\, t_c + V_{P1}[H]_{P1} + 4[N_p^{+4}]_4\, (\dot{V}_4\, t_c + V_{P1})}{\dot{V}_4\, t_c + V_{P1} + V_7}$$

Mat. Balance for [$H_2C_2O_4$] in P2

Let $B \equiv H_2C_2O_4$

2) $$[B]_{P2} = \frac{V_7[B]_7 + [B]_4\, \dot{V}_4\, t_c + V_{P1}[B]_4 - 2[N_p^{+4}]_4(\dot{V}_4\, t_c + V_{P1})}{\dot{V}_4\, t_c + V_{P1} + V_7}$$

knowing $R_s = \dfrac{[B]}{[H]^2}$

3) $$(R_s)_{P2} * \left[\frac{V_7[HNO_3] + [HNO_3]_4\, \dot{V}_4\, t_c + V_{P1}[HNO_3]_{P1} + 4[N_p^{+4}]_4\, (\dot{V}_4\, t_c + V_{P1})}{\dot{V}_4\, t_c + V_{P1} + V_7}\right]^2$$

$$= \left[\frac{V_7[H_2C_2O_4]_7 + [H_2C_2O_4]\, \dot{V}_4\, t_c + V_{P1}[H_2C_2O_4] - 2[N_p^{+4}]_4\, (\dot{V}_4\, t_c + V_{P1})}{\dot{V}_4\, t_c + V_{P1} + V_7}\right]$$

where: $t_c \equiv$ cycle time of process, 60 min.

33) $[B]_{P1} = [B]_{P1}^{o} \exp - \left(\dot{V}_4 t/V_{P1}\right) + \left[\dfrac{\dot{V}_3[B]_3 + \dot{V}_8[B]_8 - 2\,\dot{V}_{1B}\,[N_p^{+4}]_{1B}}{\dot{V}_4}\right] *$

$$\left[1 - \exp - \left(\dot{V}_4 t/V_{P1}\right)\right]$$

where $[B]_{P1} = [B]_{P1}^{o}$ @ $t = 0$

i.e., the initial concentration of oxalic acid in P1 prior to precipitation.

Material Balance for $[Np]_{P1}$ in P1

34) $\qquad \left(\dot{M}_{Np}\right)_i - \left(\dot{M}_{Np}\right)_o - \left(\dot{M}_{Np}\right)_{RXN} = \dfrac{d(M_{Np})_{P1}}{dt}$

For the analysis of $[Np]_{P1}$ it is beneficial to examine the case of the instantaneous mixed condition (IMC). The instantaneous mixed condition represents the system conditions prior to precipitation.

The instantaneous mixed condition is present during an infinitisimal period of time.

35) $\dot{V}_{1A}[N_p^{+4}]_{1A} + \dot{V}_3[N_p^{+4}]_3 + \dot{V}_8[N_p^{+4}]_8 - \dot{V}_4[N_p^{+4}]_4 = \dfrac{d\left(V_{P1}[N_p^{+4}]_{P1}\right)}{dt}$

$\qquad\qquad [N_p^{+4}]_{P1}^{o} = 0$ @ $t = o$

Assuming: $\quad [N_p^{+4}]_4 = [N_p^{+4}]_{P1}$

$\qquad\qquad [N_p^{+4}]_3 \equiv$ negligible

the following equation results

$$36) \quad [N_p]_{P1}^{IMC} = \frac{\dot{V}_{1B}[N_p^{+4}]_{1B}}{\dot{V}_4} \left(1 - \exp \ -\left(\dot{V}_4 \ t/V_{P1} \right) \right)$$

In the case of the oxalate material balance (Equation 33) it was essential to consider the consumption of oxalate ion ($C_2O_4^{-2}$) by the precipitation reaction. Since the equilibrium solubility is a function of the free oxalate concentration, consideration of this stoichiometric consumption is necessary to control the solubility during precipitation. The amount of Np^{+4} in solution at post precipitation conditions is dictated by the equilibrium solubility.

The instantaneous mixed condition (IMC) merely provides a quantitative measurement of the total amount of Np present in Pl before precipitation occurs. Therefore, the analysis of the IMC for Pl assumes $(\dot{M}_{Np})_{RXN} = 0$ in Equation 34.

At steady-state conditions, Equations 33 and 30 reduce to the following:

$$37) \quad [B]_{P1}^{SS} = \frac{\dot{V}_3 \ [B]_3 + \dot{V}_8 [B]_8 - 2 \ \dot{V}_{1B} \ [N_p^{+4}]_{1B}}{\dot{V}_{1B} + \dot{V}_8 + \dot{V}_3}$$

$$38) \quad [H]_{P1}^{SS} = \frac{\dot{V}_{1B} \ [H]_{1B} + \dot{V}_8 [H]_8 + \dot{V}_3 [H]_3 + 4[N_p^{+4}]_{1B} \ \dot{V}_{1B}}{\dot{V}_3 + \dot{V}_8 + \dot{V}_{1B}}$$

; where $\dot{V}_4 = \dot{V}_3 + \dot{V}_8 + \dot{V}_{1B}$

Using these two equations and the solubility parameter, we find that:

$$39) \quad \left[\frac{\dot{V}_3 [H_2C_2O_4]_3 + V_8 [H_2C_2O_4]_8 - 2 \ \dot{V}_{1B} [N_p^{+4}]_{1B}}{\dot{V}_3 + \dot{V}_8 + \dot{V}_{1B}} \right] =$$

$$(R_s)_{P1} \left[\frac{\dot{V}_{1B} [HNO_3]_{1B} + \dot{V}_8 [HNO_3]_8 + \dot{V}_3 [HNO_3]_3 + 4[N_p^{+4}]_{1B}}{\dot{V}_3 + \dot{V}_8 + \dot{V}_{1B}} \right]^2$$

Material Balance for $[C_6H_8O_6]$ in the primary precipitator

Let $\quad A \equiv C_6H_8O_6$

40) $\quad (\dot{M}_A)_i - (\dot{M}_A)_o + (\dot{M}_A)_{gen} = \dfrac{d(M_A)_{P1}}{dt}$

41) $\quad \dot{V}_{1B}[A]_{1B} + \dot{V}_3[A]_3 + \dot{V}_8 [A]_8 - \dot{V}_4[A]_4 = \dfrac{d(V[A])_{P1}}{dt}$

Assume: $\quad (\dot{M}_A)_{gen} = [A]_8 = [A]_{P1}^O = 0$

$\qquad\qquad [A]_{P1} = [A]_4$

42) $\quad \dot{V}_{1B}[A]_{1B} + \dot{V}_3[A]_3 - \dot{V}_4[A]_{P1} = V_{P1} \dfrac{d [A]_{P1}}{dt}$

Performing the same mathematical excercises for Equation (42) as for Equation (3) one finds:

43) $\quad [A]_{P1} = \left[\dfrac{\dot{V}_{1B}[A]_{1B} + \dot{V}_3[A]_3}{\dot{V}_{1B} + \dot{V}_3 + \dot{V}_8} \right] * \left[1 - \exp \left(\dfrac{-\dot{V}_4 \, t}{\dot{V}_{P1}} \right) \right]$

44) $\quad [A]_{P1}^{SS} = \left[\dfrac{\dot{V}_{1B} [A]_{1B} + \dot{V}_3 [A]_3}{\dot{V}_{1B} + \dot{V}_3 + \dot{V}_8} \right]$; steady-state concentration of ascorbic acid

The results of these calculations are shown in Figure 10.